

**Absorptively-electrochemical method of air purification from hydrogen sulfide at the municipal  
solid wastes processing plants**

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### **Abstract**

Absorptively-electrochemical method is proposed to use for air and water purification from hydrogen sulfide on MSW landfills. The experimental stand for air purification from hydrogen sulfide was created on the basis of absorptively-electrochemical method. Schematic diagram of the experimental stand for air purification from hydrogen sulfide is shown. Kinetics of hydrogen sulfide oxidation in a closed circuit of experimental stand at relative air humidity 95% is shown. The research results of hydrogen sulfide absorption by oxygen-saturated water are obtained on the basis of experiment. The main indicators influencing the efficiency of air purifying process from hydrogen sulfide were determined. A general view of absorptively-electrochemical setup for air purification from hydrogen sulfide is shown.

**Keywords:** hydrogen sulfide, absorption, the instantaneous chemical reaction, mass exchange apparatus, electrochemical reactor.

**Introduction.** A large amount of harmful gases is released into the environment as a result of decay of municipal solid wastes (MSW). These gases include mercaptans, carbon dioxide, methane, ammonia, hydrogen sulfide [Sasson 1985]. For example, hydrogen sulfide maximum permissible concentration (MPC) is significantly exceeded (more than 10 MPC) in the air of MSW landfills in Voronezh, Liski and Rossosh [Ашихмина 2014]. The researches [Сметанин 2013] have shown that increasing of phosphogypsum concentration in biogas leads to an increase of H<sub>2</sub>S concentration from 138,8 mg/m<sup>3</sup> to 348,3 mg/m<sup>3</sup>. The calculations of hydrogen sulfide emissions can contain up to 1.5% of the total emissions of gases from existing MSW landfills of Donetsk and Makeyevka in "landfill gas" [Краснянский 2004]. The rate of H<sub>2</sub>S formation can reach 0,5·10<sup>-2</sup> (mg/m<sup>3</sup>) per day according to investigation of kinetics of H<sub>2</sub>S formation based on MSW model mixture [Краснянский 2006]. The hydrogen sulfide emissions are 120 kg/year from MSW landfill depositing in Svetly township in Saratov region [Шыхмамедова 2013].

The hydrogen sulfide MPC according to [Инструкция по проектированию, эксплуатации и рекультивации полигонов для ТБО 1996]: maximum single - 0,08 mg/m<sup>3</sup>, in the personnel working zone - 10,0 mg/m<sup>3</sup>.

Regulatory requirements for hydrogen sulfide concentration in the air are sufficiently rigid. Hydrogen sulfide concentration in the MSW landfills air [Ашихмина 2014, Сметанин 2013, Краснянский 2004, Шыхмамедова 2013] is much higher than the established norms [Инструкция по проектированию, эксплуатации и рекультивации полигонов для ТБО 1996]. Furthermore, hydrogen sulfide is a substance belonging to the second hazard class. Therefore a matter of H<sub>2</sub>S removing from the MSW air and water is relevant and necessary in order to ensure human health and environmental protection.

MSW landfills infrastructure does not allow using sophisticated equipment for water and air purification from hydrogen sulfide. Therefore it is advisable to perform the analytical assessment of the

efficiency of hydrogen sulfide oxidation by atmospheric oxygen in water. The water absorbs oxygen during contact with air. Thus hydrogen sulfide is oxidized in water to the colloidal sulfur and sulfur dioxide. There are a lot of works devoted to the hydrogen sulfide oxidation in the water by air oxygen. Data of the most comprehensive researches are shown in Table 1.

Table 1. The results of H<sub>2</sub>S oxidation researches

Water type	Parameter that assesses the duration or purification efficiency	Source
Natural water	The half-life $t_{1/2}=50\pm 16$ h	[O'Brien 1977, Millero 1986]
Sea water	The half-life $t_{1/2}=26\pm 9$ h	[Millero 1987, Chen 1972]
The sodium salts aqueous solution	The duration of oxidation $t=24$ h	[Алферова 1969]
Brine water	The degree of H <sub>2</sub> S conversion $\eta=45\%$ (per 30 min)	[Кочеткова 1985]

The data analysis shows that intensity of H<sub>2</sub>S oxidation by atmospheric oxygen is low for the conditions described in [O'Brien 1977, Millero 1986, Millero 1987, Chen 1972, Алферова 1969]. In our opinion this is connected with the lack of surface of phases contact and small diffusion coefficients of oxygen and hydrogen sulfide in water. Our investigations [Лейбович 2013] of the possibility of hydrodynamic intensification processes of H<sub>2</sub>S oxidation by atmospheric oxygen showed that using rotary-vortex devices allows achieving water droplets size less than 100 microns. But thus it became clear that we need the deeper investigations of mass transfer processes of air and water purification from hydrogen sulfide based on the Higbee's theory.

**Materials and methods.** H<sub>2</sub>S absorption investigations were carried out on the basis of experimental stand for air purification from hydrogen sulfide within the framework of absorptively-electrochemical method. Schematic diagram of the experimental stand is shown in Fig.1

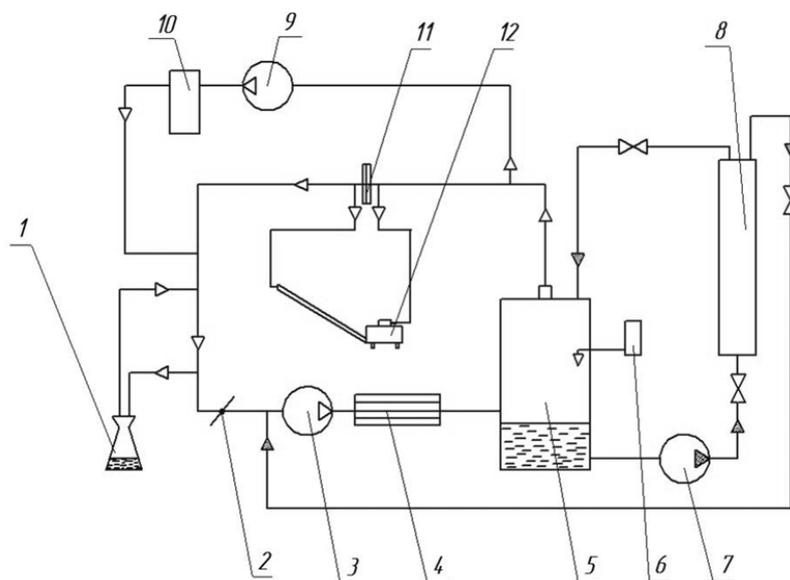
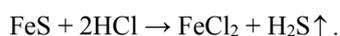


Fig.1 Schematic diagram of the experimental stand for air purification from hydrogen sulfide:  
 1 - hydrogen sulfide receiving container; 2 - damper; 3 - mass transfer device; 4 - slot separator;  
 5 - tank; 6 - sorbent doser; 7 - pump; 8 - the electrochemical reactor (ECR); 9 - compressor;  
 10 - gas analyzer; 11 - diaphragm 12 – micromanometer

Hydrogen sulfide obtaining is carried out in a specially designed dispenser based on the reaction:



Experimental stand has a closed circuit. The generated hydrogen sulfide is mixed with air in the circuit. H<sub>2</sub>S dosage stops when necessary concentration of this gas is achieved. Gas circulation in the circuit is performed by mass transfer device 3. Air consumption adjustment is made by means of damper 2. Absorbent from ECR 8 is supplied to the suction inlet of mass transfer device 3. Absorbent fragmentation into finely dispersed droplets in mass transfer device 3 creates a large surface of phases contact. The more surface of phases contact the higher purification efficiency. Then the gas is supplied to the slot separator 4. Slot separator 4 is used for separation of finely dispersed liquid particles. Then the separated liquid and the gas are supplied into the tank 5. The H<sub>2</sub>S absorption products are pumped in the

ECR 8, wherein the absorbent regeneration is performed. The H<sub>2</sub>S concentration is measured by a gas analyzer 10. Compressor 9 is used for the gas supplying to the gas analyzer sensor. Pressure difference across the diaphragm 11 is measured by micromanometer 12 in order to determine the air flow rate.

The following basic reactions take place between H<sub>2</sub>S, O<sub>2</sub> and SO<sub>2</sub> [Гончаров 2010]:



The kinetics of each of the above chemical reaction can be described by the following equation [Панченков 1985]:

$$k = \frac{1}{\tau} \cdot \ln \frac{C_0}{C},$$

$\tau$  - current time value, sec.;  $C_0$  - initial concentration of the substance, mg/m<sup>3</sup>;

$C$  - current concentration of the substance mg/m<sup>3</sup>.

The experiments were carried out at different initial concentrations  $C_0$  to assess the influence of H<sub>2</sub>S initial concentration on the absorption process character. The duration of each experiment ( $\tau$ ) was 30 minutes. The quantity  $dt$  on the graphs (Fig.2, Fig.3) represents the ratio of the current time ( $t_i$ ) to the duration of the experiment.

Magnitude  $dC$  is given by:

$$dC = (C_{i-1} - C_i) / C_{i-1},$$

$C_{i-1}$  – hydrogen sulfide concentration corresponding to the time  $t_{i-1}$ ;  $C_i$  – current hydrogen sulfide concentration.

The account of H<sub>2</sub>S oxidation kinetics by oxygen that is contained in the air, allows evaluating the effectiveness of air purification from H<sub>2</sub>S by any physical method. Preliminary researches were conducted in order to evaluate the impact of H<sub>2</sub>S spontaneous oxidation in the air of experimental stand closed circuit. Some results of these researches are shown in Fig. 2.

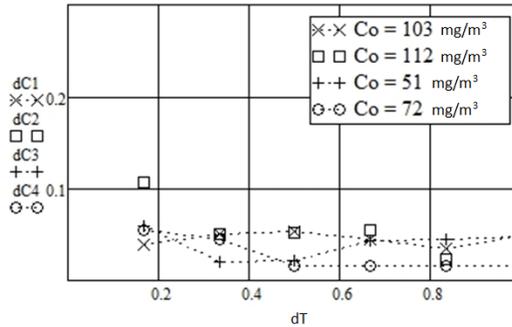


Fig. 2. Kinetics of H<sub>2</sub>S oxidation in a closed circuit of experimental stand at relative air humidity 95%

Literature data analysis shows that evaluation data of H<sub>2</sub>S oxidation kinetics directly by oxygen into the air space is not enough. Preliminary assessment of the H<sub>2</sub>S oxidation by oxygen can be made on the basis of sodium sulfide oxidation data [Кочеткова 1985]. The following regression dependence was obtained on the basis of data processing [Кочеткова 1985]:

$$\frac{dC}{dT} = \frac{0,15}{T^{0,7}} - 0,02,$$

$dC=c/c_H$  - sodium sulfide relative concentration in the test solution,  $c$  - current value of the sodium sulfide concentration, mg/m<sup>3</sup>;  $c_H$  - initial value of sodium sulfide concentration, mg/m<sup>3</sup>;  $T= \tau/\tau_e$  - relative time of experiment,  $\tau$  - current experience time, sec.;  $\tau_e$  - total duration of experience, sec.

The character of hydrogen sulfide oxidation by air oxygen (Fig. 2) coincides with the data of sodium sulfide oxidation [Кочеткова 1985]. The chemical reaction of sodium sulfide oxidation is a single stage. Thus it can be assumed that hydrogen sulfide oxidation by air oxygen is mostly goes with the formation of SO<sub>2</sub>.

Some research results of H<sub>2</sub>S absorption by oxygen-saturated water are shown in Fig. 3.

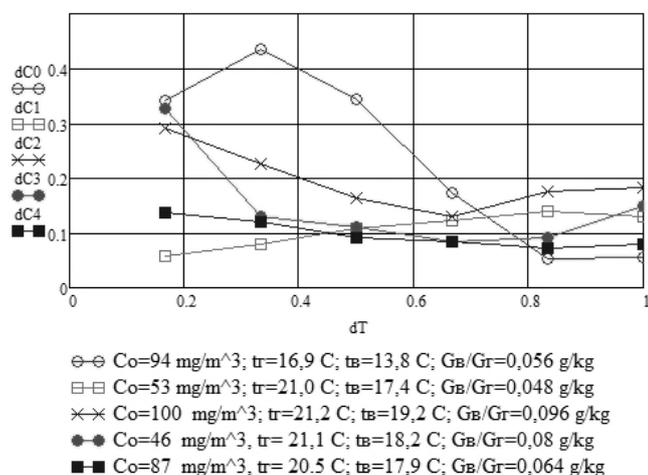


Fig. 3. The dependence of H<sub>2</sub>S absorption efficiency by oxygen-saturated water from the experiment duration

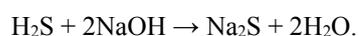
Temperature ( $t_b$ ) and water volume used for absorption ( $G_B/G_r$ ) are the main indicators influencing the efficiency of air purifying process from H<sub>2</sub>S. First of all, the variations in the character of H<sub>2</sub>S oxidation kinetics associated with H<sub>2</sub>S absorption kinetics by water and kinetics of chemical reaction between H<sub>2</sub>S and SO<sub>2</sub> (Claus process) [Гончаров 2010]. The equilibrium state of absorption kinetics and chemical reactions (1) and (2) is reached after 15...20 minutes of contact between the dispersed water and air. Then the H<sub>2</sub>S oxidation efficiency depends on one parameter (the temperature of the process).

The higher efficiency of H<sub>2</sub>S oxidation at the initial stage of the experiment explained by the fact that water is not yet saturated by reaction (2) products. Therefore it becomes necessary to intensify the process of H<sub>2</sub>S oxidation in the water.

Calcium and magnesium ions provide some catalytic effect on the H<sub>2</sub>S oxidation reaction [Леонов 1987]. The strong catalytic effect of ions of some metals (especially nickel and cobalt) provides the ability to control the H<sub>2</sub>S oxidation reaction.

The absence of the regeneration cycle of H<sub>2</sub>S oxidation catalyst reduces its catalytic properties. Electrochemical processing is one of the most rational processes of the catalytic properties recovery.

**Results and discussion.** Absorptively-electrochemical method is proposed to use by the authors for air purification from hydrogen sulfide and also removing odors. The essence of this method is simple. As a starting material for hydrogen sulfide absorbent producing is used an aqueous sodium chloride solution. The alkali is formed at the cathode during the electrolysis process. This alkali is used in mass transfer apparatus for hydrogen sulfide absorption from the air in one of the following reactions:



Then the reaction products are served to the electrochemical reactor, where the absorbent (alkali) is regenerated.

A general view of absorptively-electrochemical setup of air purification from hydrogen sulfide is shown in fig. 4.

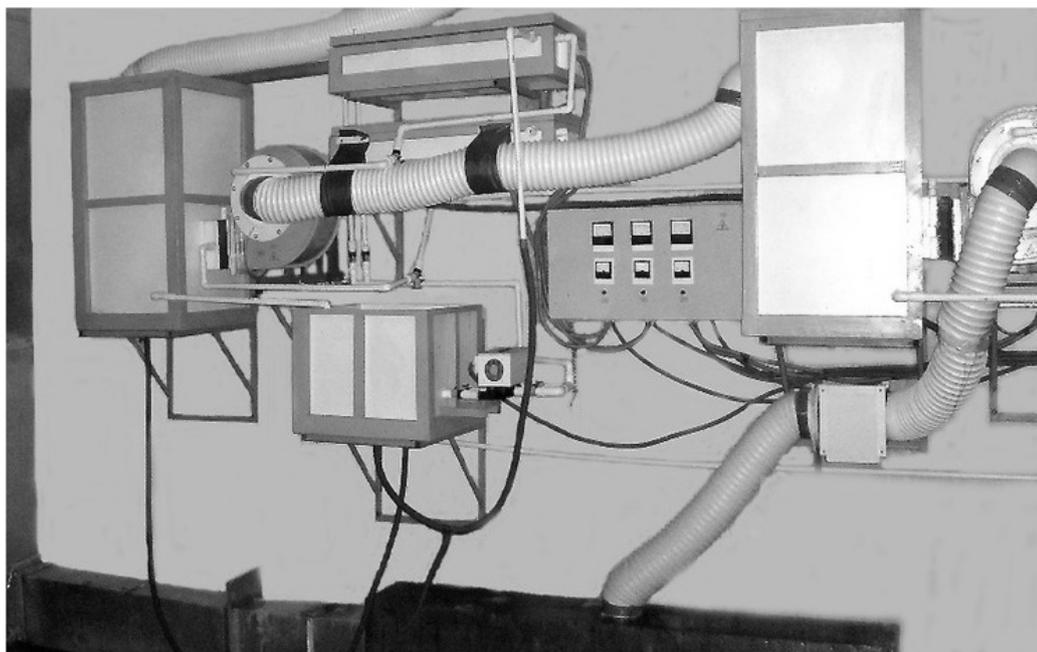


Fig. 4. Absorptively-electrochemical setup of air purification from hydrogen sulfide

The main advantage of absorptively-electrochemical method is the lack of necessity to use a large amount of expensive reagents, because required absorbents can be prepared from the aqueous sodium chloride solution and then regenerating them in the electrochemical reactor. Filtering water contains a large amount of dissolved salts of metals, including those which are strong catalyts of hydrogen sulfide oxidation. Therefore there is no need to use reagents for filtering water purification at the MSW landfills. The major costs in this method are electricity.

Also important to note that during the studying hydrogen sulfide absorption process by various sorbents [Astarita 1967], it was found that hydrogen sulfide absorption takes place in instantaneous reaction mode. The dependence between the velocity of instantaneous reaction plane displacement deep into absorbent drop and time of his contact with hydrogen sulfide was obtained on the basis of literature data [Sherwood 1975] processing. Taking into account the time of existence of sorbent droplets that is spattering into the mass exchange apparatus, this velocity exceeds 300 m/s. It indicates at the high speed of absorption process and, therefore, at the high purification efficiency that reaches to 99.9%.

The annual tests of absorptively-electrochemical setup efficiency show that hydrogen sulfide is absent in the room where this setup is located. H<sub>2</sub>S concentration at the exit from the setup does not exceed 3 mg/m<sup>3</sup>.

### **Conclusions.**

1. Absorptively-electrochemical method is expedient to use for air and water purification from hydrogen sulfide on MSW landfills.
2. The catalyts of hydrogen sulfide oxidation in water can be generated directly from the salts which are dissolved in MSW landfills water.
3. The electrochemical method can be used for regeneration of H<sub>2</sub>S oxidation catalyts to the required level.

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